SOME ELECTRICAL PROPERTIES OF SILVER SULPHIDE

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1. INTRODUCTION

In the course of another investigation the author was led to examine some of the electrical properties of silver sulphide. It was found that the sulphide could be rolled into thin strips or drawn into short wires like a metal. The electrical behavior of the sulphide is peculiar. It is properly to be classed as a pyroelectric [1] conductor, but it possesses certain characteristics which further study may show to be useful in various practical applications. In the form of a strip it is both a metallic and electrolytic conductor at the same time, but it may be prepared as a metallic conductor of negligible temperature coefficient. Observations have been made on its resistance to alternating and direct current, its volt-ampere characteristics, its specific resistance, its electrochemical decomposition, etc. The results of only a part of the experiments which were planned are contained in this paper, which is published now because it does not appear possible to continue the investigation on account of the pressure of other duties.

2. PREPARATION OF SPECIMENS

The native silver sulphide, argentite, is seldom pure, but silver sulphide may be prepared chemically in the form of a black powder. This powder may be fused in a porcelain crucible by means

[1] Steinmetz, General Electric Review, 19, p. 362; 1916.

of a blast lamp. The melting point is about 825° C, according to Pelabon.[2] It is necessary to keep the crucible tightly covered during the fusion to prevent the oxidation of the sulphur by the air, with the consequent liberation of metallic silver, which becomes plainly visible if any considerable amount is formed. The fused mass after cooling resembles gun metal in color. It is sufficiently malleable to permit the fused button to be rolled by small steps into a strip. In doing this the sulphide "cries" like tin and cracks along the edges somewhat worse than crystalline zinc. At a higher temperature (about 200°) it becomes very malleable and may be hammered out on a hot plate or drawn through a heated drawplate into short wires. Such working of the material changes its electrical properties, as will be shown later. Analysis of the fused sulphide, by Mr. Scherrer, showed about 3 per cent free silver over that corresponding to the formula Ag_2S, and slight traces of silica and iron.

For making experiments on the sulphide it was necessary to have some means of making good electrical and mechanical contact between the sulphide and copper wires. It has not been found possible to solder to the sulphide directly, and brass clamps are not desirable, but it is possible to silver plate the ends of a piece of the sulphide in a silver-potassium-cyanide solution. After this is done the sulphide can be soldered to the copper wire with comparatively little difficulty. The principal precaution to be observed in the soldering is to avoid overheating the sulphide.

3. METALLIC AND ELECTROLYTIC CONDUCTION

Bädeker [3] found that below 175° the sulphide is an electrolytic conductor and above this temperature it is a metallic conductor, the transition being marked by an abrupt change in the electrical resistance as the temperature passed this point in either rising or falling. His specimens were prepared by sputtering thin films of silver on glass or mica and then converting the silver into sulphide. In this respect Bädeker's work has little bearing on the present investigation. Other papers dealing with this sulphide note that it has a high temperature coefficient of resistance.

(*a*) *Temperature Coefficient.*—In the present investigation it was found that a strip of the sulphide rolled at room temperature showed a large negative temperature coefficient of resistance, but it was difficult to repeat the readings with exactness, although

[2] Comp. Rend., 143, p. 294.

[3] Ann. d. Phys., 327, p. 758; 1907.

the strip was in an oil bath. A short wire of the sulphide drawn through a drawplate at about 200° was observed at eight temperatures in the range 18° to 31°, with the result that the temperature coefficient was found to be zero. The explanation of this difference, as deduced from other observations, appears to be that the strip rolled at room temperature conducts the current both metallically and electrolytically at the same time, while the wire is a metallic conductor. The large temperature coefficient of the strip was due to the electrolytic conduction.

It is not easy to explain why mechanical working of a substance such as this makes so radical a change in electrical properties, but it seems likely that rolling the sulphide at room temperature may produce minute cracks. The wire which was drawn hot is probably homogeneous, due to the mechanical working. It was thought that if a strip of the sulphide were put in a vacuum it might lose its electrolytic properties, but this did not prove to be the case. A strip, with fine copper conducting leads, was sealed in a desiccator over phosphorous pentoxide and evacuated as far as possible with an oil pump. After several hours in the vacuum measurements were made, but no change in the peculiar behavior (described in the next section) of the strip could be detected. After standing over night it was found that the resistance had increased greatly and visible decomposition of the sulphide had begun. It had lost its metallic luster entirely.

(*b*) *Comparison of Alternating and Direct-Current Resistance.*— One of the earliest experiments made was a comparison of the resistance of the specimens on alternating and direct current. It was found that the resistance of the strip rolled at room temperature was usually higher for the alternating-current measurements than for the direct current. To eliminate the possibility that this effect might be due to temperature changes, the specimens were mounted in a thermostatic oil bath controlled to 0.01° and vigorously stirred. A special bridge was arranged to make measurements on either alternating or direct current by merely throwing a switch and interchanging a telephone and galvanometer. The measurements could therefore be made under similar conditions and nearly simultaneously, but the result was the same as before. Measurements made on the hot-drawn wire did not, however, show these peculiarities of the strip. Its resistance with direct and alternating current was always the same.

Although the bridge currents were very small, it was found that the use of the alternating current produced steadily increas-

ing values of resistance while the direct current decreased the values of the resistance. As successive measurements were made the resistance with alternating and direct current differed more and more. This effect was also produced when a small auxiliary alternating (60 cycles) or direct current was passed through the specimen for a few seconds or a minute and then the resistance measurements made. An increase in resistance always resulted from the passage of the alternating current and a decrease from the direct current. Fig. 1 shows the effect of 8.8, 14, and 18.6 milliampere, 60-cycle alternating current applied for one-minute intervals, as indicated by the double lines. During the periods

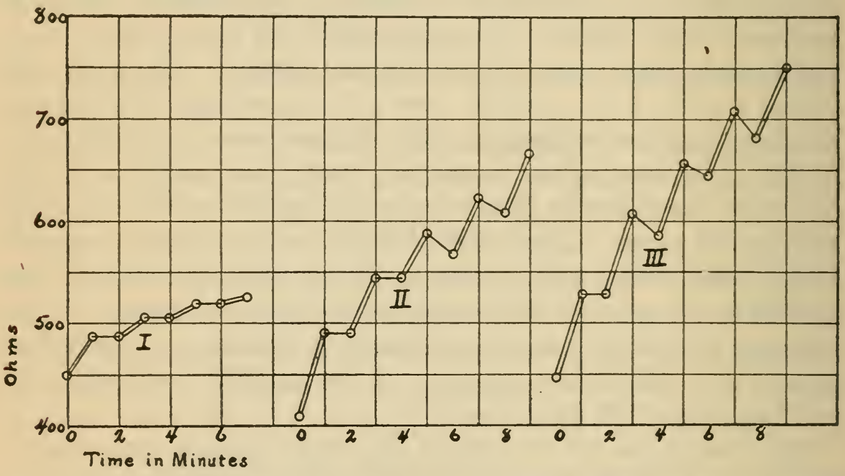

Fig. 1.—*Resistance of a strip of silver sulphide as affected by a small alternating current. An Alternating current of 60 cycles was passed through the sulphide for one-minute intervals as indicated by the double lines. Resistances were measured on an alternating-current bridge. The current for curve I was 8.8 ma; for II, 14.0 ma; for III, 18.6 ma*

denoted by the single lines only the bridge current of about 5 milliamperes was flowing through the specimen. The downward direction of the single lines in the upper part of curves *II* and *III* of Fig. 1 and the upward direction of the single lines in the *D. C.* curve of Fig. 2 show that the effect produced is not a permanent one. Complete recovery is often a matter of considerable time.

After making these observations it was found that Fitz Gerald [4] had previously observed similar differences in resistance on alternating and direct current, but the explanation which he gives does not seem to fit the present observations noted at top of page that successive measurements of resistance made alternately and

[4] Trans. Am. Electrochem. Soc. 25, p. 393, 1914.

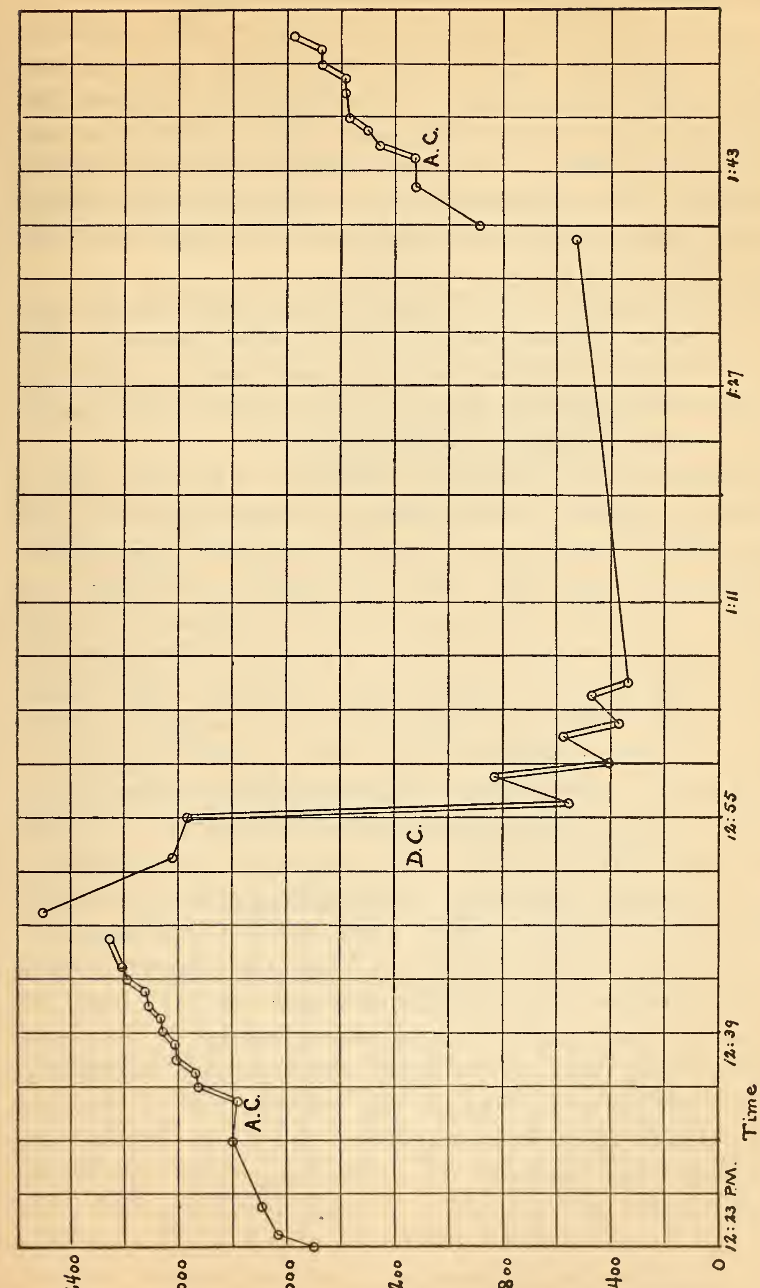

FIG. 2.—*Resistance of a strip of silver sulphide as affected by small alternating and direct currents. A 60-cycle alternating current of 19 ma was passed through the strip for 10-second periods during the latter part of the intervals indicated by the double lines of the 1st and 3rd curves. Similarly a direct current of 30 ma was passed through the strip for 10-second periods of the middle curve*

in rapid succession with alternating and direct current differed more and more as each new measurement was made.

Fig. 2 gives somewhat similar results for another specimen (strip) of the sulphide. These results do not show quite the perfect regularity of those in Fig. 1, but are given to illustrate the contrasting effects of alternating and direct currents on the sulphide. This specimen was in the large oil bath, thermostatically controlled. The measurements on alternating and direct current were made in quick succession, as will be noted from the time scale, time being plotted as abscissa.

Experiments similar to the foregoing were tried with the wire which was drawn hot, but no such effects were observed. The alternating and direct current measurements were in agreement, and no effect was produced when auxiliary currents were passed through it. The wire behaved like a metal.

It is possible that the decrease in resistance of the strip when a direct current is passed through it may have some relation to the "voltage effects"[5] noted in the case of selenium and stibnite cells. Steinmetz[6] says that some pyroelectric conductors have the property that their resistance increases permanently, often by many hundred per cent, when the conductor is for some time exposed to high-frequency electrostatic discharges. The observations of the present paper indicate that silver sulphide is sensitive to low frequency and that it may recover its former value.

(*c*) *Volt-Ampere Characteristic.*—The volt-ampere characteristic of a strip in air (4.7 by 0.4 by 0.007 cm) was measured with both alternating and direct currents. It was found to be similar to that of a pyroelectric conductor. Some difficulty was encountered in making the alternating-current measurements because of the peculiar behavior of the sulphide. When the current passing through the specimen was small the resistance was very high, but when relatively large currents were forced through it the resistance became very low. As a result the low-scale alternating-current voltmeters took most of the current, and it was not found practicable to make corrections. Mr. H. B. Brooks very kindly arranged and operated an alternating-current potentiometer to overcome this difficulty. A small correction had to be made for the current through the potential coil of the wattmeter that was also included in the circuit. The direct-current measurements were easily made. A portable galvanometer with resistance

[5] Elliott, Phys. Rev., 5, p. 53; 1915.

[6] Loc. cit.

in series was used for reading the voltage. The results of these measurements are given in Fig. 3. It was not possible to repeat the whole series of measurements on the wire, but direct-current measurements were made with the same apparatus as was used for the strip. The wire was in the thermostat bath, where it had been kept from the beginning of the experiments. The maximum current density in this specimen was 43 amperes per square centimeter. The curve (Fig. 4) is characteristic of metallic conduction, and taken in connection with the agreement of the bridge

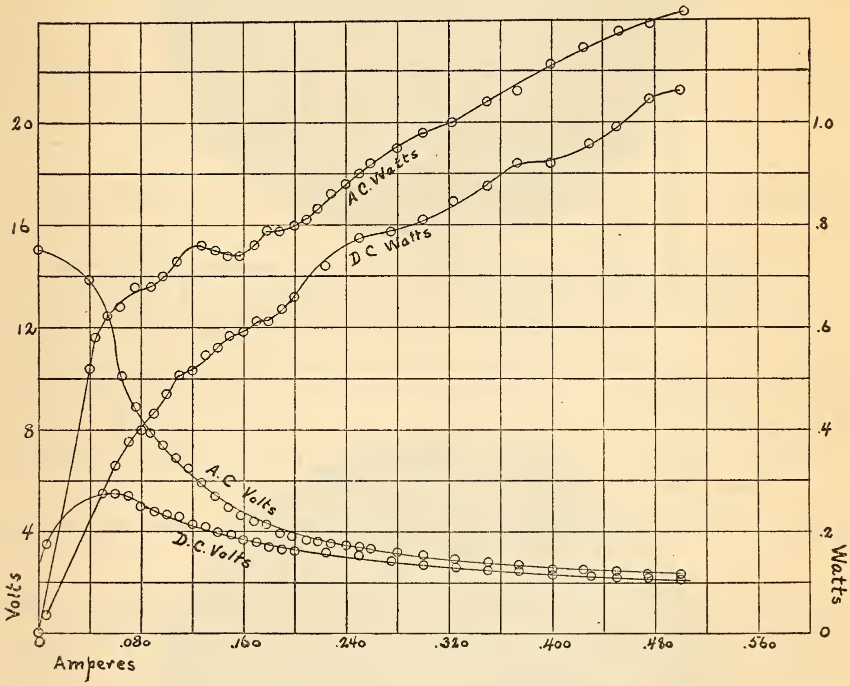

FIG. 3.—*Volt-ampere characteristic of a strip of silver sulphide on alternating and direct current*

measurements for both alternating and direct current it indicates that the sulphide drawn hot is a metallic conductor at ordinary temperatures, within the range of these experiments. The conditions for these experiments were quite different from those of the bridge measurements, the results of which are given in Figs. 1 and 2. Probably they are not as correct at the very low currents.

4. SPECIFIC RESISTANCE

Measurements were made on the wire to determine its specific resistance at 25°0 C. It was found to be 17 300 microhm-centimeters, or about 10 000 times the specific resistance of copper.

5. ELECTROCHEMICAL DECOMPOSITION

Experiments were made to find the electrochemical decomposition due to the electrolytic conduction of the strips of sulphide. A strip in air (5.5 by 0.3 by 0.01 cm) with silver-plated ends (Fig. 5) was soldered to copper leads and put in a direct-current circuit. The initial current of 25 milliamperes was passed through it for nearly an hour without visible change. The current was increased by steps of 50 milliamperes at 10-minute intervals until with 200 milliamperes a discoloration of the plating at the anode

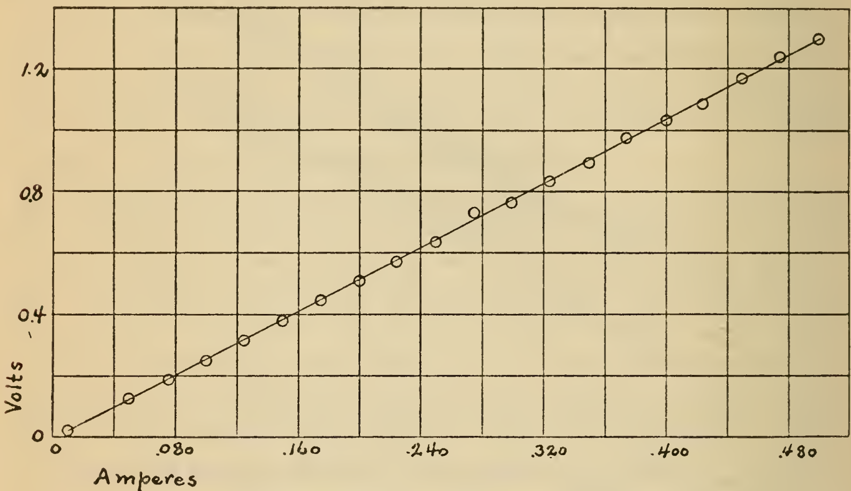

FIG. 4.—*Volt-ampere characteristic for a wire of silver sulphide drawn hot, measured with direct current*

end was noticed. A further increase to 300 milliamperes completed the destruction of the silver plating at the anode end and finally burned off the terminal, but before this happened a myriad of little shiny silver crystals appeared on the black surface of the sulphide, as shown in Fig. 6. The appearance of these crystals was carefully studied under the microscope, and it was found that they occurred even to within a small fraction of a millimeter of the anode terminal. (Fig. 7.)

They appeared in various forms, some of which suggested that they had been expelled from the interior of the sulphide by considerable force. The strip of silver sulphide appeared to be made up of a multitude of tiny electrolytic cells between which metallic conduction occurred. The appearance of the silver shown in Fig. 6 suggests a possible cause for the occurrence of native silver

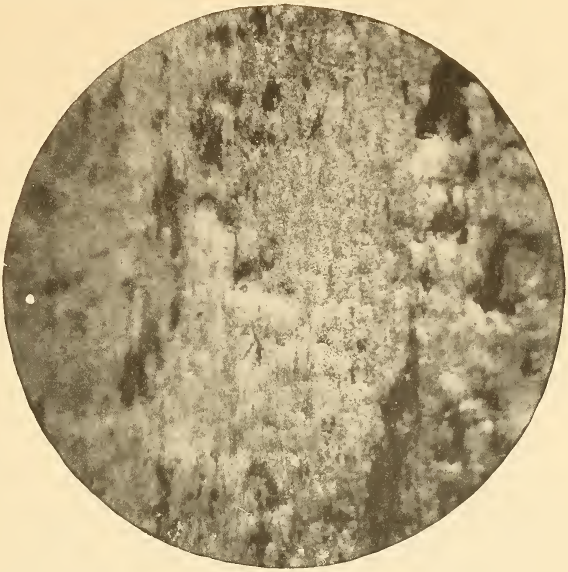

FIG. 5.—*Silver plating at cathode end of strip. No visible change took place in the plating at this end. This picture may properly represent also the appearance of the plating at the anode end before it was destroyed by electrolysis.* × 50

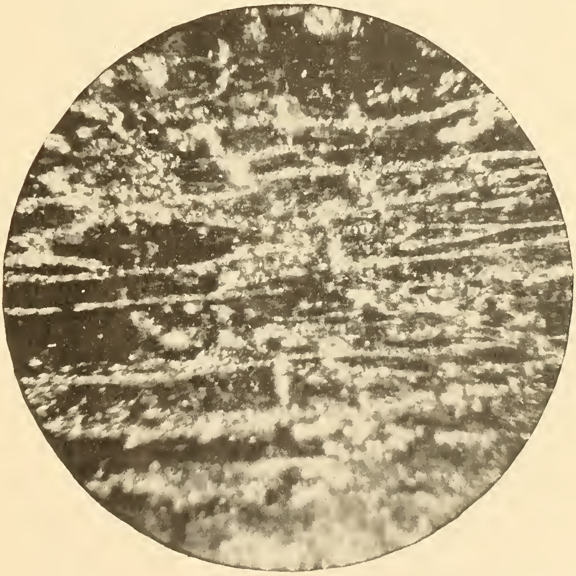

FIG. 6.—*Outcropping of silver in middle of strip due to the electric current which flowed approximately parallel to the direction of the lines of silver.* × 50

FIG. 7.—*Anode end showing where the terminal burnt off. After the silver plating was destroyed by the sulphur, the outcropping of silver took place, even within a small fraction of a millimeter of the anode end.* × 50

in argentite[7] as an electrochemical product. The lines of silver in Fig. 6 suggest veins of silver in the earth.

An experiment similar to this was carried out with alternating current, but no visible decomposition of the sulphide was observed, although the current was carried to 600 milliamperes, which was twice the direct current that completed the destruction of the other strip of sulphide.

6. MISCELLANEOUS EXPERIMENTS

Experiments were also made to determine the thermoelectromotive force of the silver sulphide against copper, but the results were inconclusive. This was probably due to the fact that a strip instead of a wire was used. The latter, if available in a long enough piece to make a suitable thermocouple, would probably show more constant values. Other experiments indicated some microphonic action when two pieces of the sulphide were pressed together and in circuit with a telephone receiver and battery.

No data have been obtained as to the stability of silver sulphide. Clarke[8] says that it is less stable than the sulphides of copper, lead, and mercury, and quotes Thomsen's values for the heat of formation of these sulphides, showing that the heat of formation of silver sulphide is only about one-fourth of that for lead sulphide.

7. SUMMARY

Silver sulphide may be prepared in the form of short wires or thin strips like a metal. The wire which must be drawn hot, has been found to conduct electricity like a metal of high specific resistance and practically zero temperature coefficient. The strip of sulphide, rolled at room temperature, has a large temperature coefficient and shows both metallic and electrolytic conduction at the same time. It has a volt-ampere curve characteristic of a pyroelectric conductor. The resistance of these strips has been examined with both alternating and direct current, with the result that the alternating-current resistance was nearly always found to be higher than that with the direct current, and the passage of a small alternating current of a frequency as low as 60 cycles increased temporarily the resistance of the sulphide, while a small direct current produced the opposite effect.

WASHINGTON, June 26, 1917.

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[7] Clarke, Data of Geochemistry, p. 559.

[8] Data of Geochemistry, p. 561.